

Remarks

The claims were rejected as being anticipated by or obvious in view of Pennsylvania Department of Environmental Protection "Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania" and, in particular, Figure 7.12. Applicant respectfully traverses because Figure 7.12 does not teach or suggest each of the limitations required by the claims.

The method of the present invention provides a means by which an operating biological heap may be simulated. For example, in the claimed method, the leaching process may be initiated by irrigating the material representative of the ore within the housing. Gas including oxygen and carbon dioxide can be supplied to the housing. The oxidation process gives rise to zones of different temperatures inside the material with the temperature of each zone being related to the leaching activity in the zone (see para. [0042]). The claimed process further requires monitoring the localized temperature at a plurality of locations (i.e., at a plurality of zones) and **in response to the monitored temperatures**, controlling heat loss from the confined volume.

As further claimed in the dependent claims and as further explained in the specification, each "temperature measurement is applied to the control system 48 which, in turn, controls the supply of electrical energy from the supply 54 to the various elements 50 to force the temperature gradient inside the column, in a transverse direction, at each of the segments which are being separately controlled, effectively to zero. This stops heat transfer out of the column to atmosphere." (para. [0042]).

Alternatively, "by varying the compositions and the flow rates of the liquid and gas supplied to the material 72 from the sources 66 and 80 respectively, it is possible to influence the leaching activity inside the column and thereby simulate leaching inside a commercially operated heap. The establishment, maintenance and variation of one or more relatively high temperature zones in the column can be effected by judicious control of the process parameters (gas and liquid compositions and flow rates) prevailing in the ore in the column. This is done in an interactive or feedback mode with the temperature control to ensure that heat loss from the column is at all times limited". (para. [0052]).

It is this feature that distinguishes the claimed method from that of Figure 7.12. Figure 7.12 shows a constant temperature leaching column. Further details of this column can be found in Cathles, L. M. and K.J. Breen, *Removal of Pyrite From Coal By Heap Leaching*, Pennsylvania State University (1983) (Final Report on Research Grants G5105007, G51115007, and G1115427; Bureau of Mines Open File Report 138-83). Pages 44-52 and appendix E pages E-1 through E-14 are attached at Tab 1 for the Examiner's convenience. Cathles describes the column in Figure 7.12 relied upon by the Examiner. The column in Figure 7.12 is a Plexiglas column (3 inch ID) wrapped with copper tubing and maintained at constant temperature by passing water from a thermal bath through the tubing (p. 44 of Cathles). The temperature was monitored at several locations along the column (*Id.*). The column apparatus was designed so that a constant temperature could be maintained throughout the interior of the column (E-4,

first line, last paragraph). This was accomplished by providing copper tubing tightly coiled around the column so that water could then be circulated from a constant temperature bath (last paragraph of E-4).

Figure 7.12 does not disclose, teach, or suggest all of the limitations required by the claims. In particular, Figure 7.12 does not teach or suggest the claimed step of controlling heat loss in response to the monitored temperatures. In fact, Figure 7.12 teaches away from such a step by simply requiring a constant temperature bath to provide a constant temperature along the axial longitudinal length of the column. Put another way, Figure 7.12 teaches providing a column so that a constant temperature could be maintained throughout the entire length of the interior of the column.

Moreover, Figure 7.12 is completely silent about any feedback control with respect to the temperature that is monitored within the column. Cathles describes that the temperature is simply monitored continuously (see first full paragraph on E-5). The only temperature control is that with respect to the constant temperature bath, which is completely separate from the column.

Such a process according to Figure 7.12 teaches away from the claimed process, which seeks to simulate leaching in a heap. During leaching of an operating heap, the temperature may vary with the depth (or height) of the heap due to operating conditions such as leach flow rate and air flow rate. The claimed process simulates that observed behavior. The claimed process monitors the temperature of the material within the claimed housing at a plurality of locations and the monitored temperature may

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differ at each of the plurality of locations. Furthermore, the claimed process requires that, in response to the monitored temperature, the heat loss at each location is controlled so that the heat loss from the confined volume is effectively zero.

Because Figure 7.12 (and the further explanation of such provided by Cathles) does not teach or suggest each of the limitations required by the claims, Figure 7.12 cannot and does not anticipate or render obvious the present claims. The applicant respectfully requests acknowledgement of such. The Examiner is invited to contact the undersigned attorney for the Applicant via telephone at (312) 321-4276 if such communication would expedite allowance of this application.

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TAB 1

cases. The transition zone width will be about 2δ , so this observed width is in excellent agreement with the predicted δ value of 169 to 308 μm at 40°C (Table 7).

Finally we can use the observed δ value of 325 μm , a τ_C value of 1.0 mo., and τ_D value of 4.0 mo for the larger size fraction leached (the 0.7 mm δ value makes utilization of the smaller size fraction data questionable) to calculate D_E and k_{ox} from equations (3) and (6). We assume $K=0.14$ and $a_{Sulf}^R = 30$, $[O_X] = 1.4 \times 10^{-3}$. The results, extrapolated back to 20°C, are: $D_E = 8.7 \times 10^{-8}$ and $k_{ox} = 1.5 \times 10^{-6}$. These values are in excellent agreement with those inferred from the literature of 7.5×10^{-8} and 10^{-6} to 10^{-7} respectively (Table 1 and 4).

4. Summary and Conclusions.

The kettle experiments confirm the activation energies, rate constants, and reaction stoichiometry deduced from the literature in the previous section. k_{ox} seems to be on the high end of the range we identified from the literature. $a_{Sulf}^R = 100 \text{ cm}^{-1}$ appears preferable to 30 cm^{-1} . Leached rims were observed as it was predicted they should be and the width of the transition zone between leached and unleached coal is about the thickness predicted. The kettle experiments provide excellent confirmation of the shrinking core leaching model.

E. Model Verification and Parameter Calibration by Column Leaching Experiment.

Four 356-422 day column leaching experiments were carried out to further test the shrinking core heap leaching model. Flexiglass columns (three inch ID) were wrapped with copper tubing and maintained at constant temperature by passing water from a thermal bath through the tubing (see Figure 10). The columns were charged with about 2.5 kg of coal, and the coal was leached by passing air at a measured rate up through the column. The leach products were periodically flushed from the columns with batches of acidified water. The cumulative oxygen extracted and iron produced by the column was monitored, as was temperature at several locations along the column. Complete details of the operation are given in Appendix E.

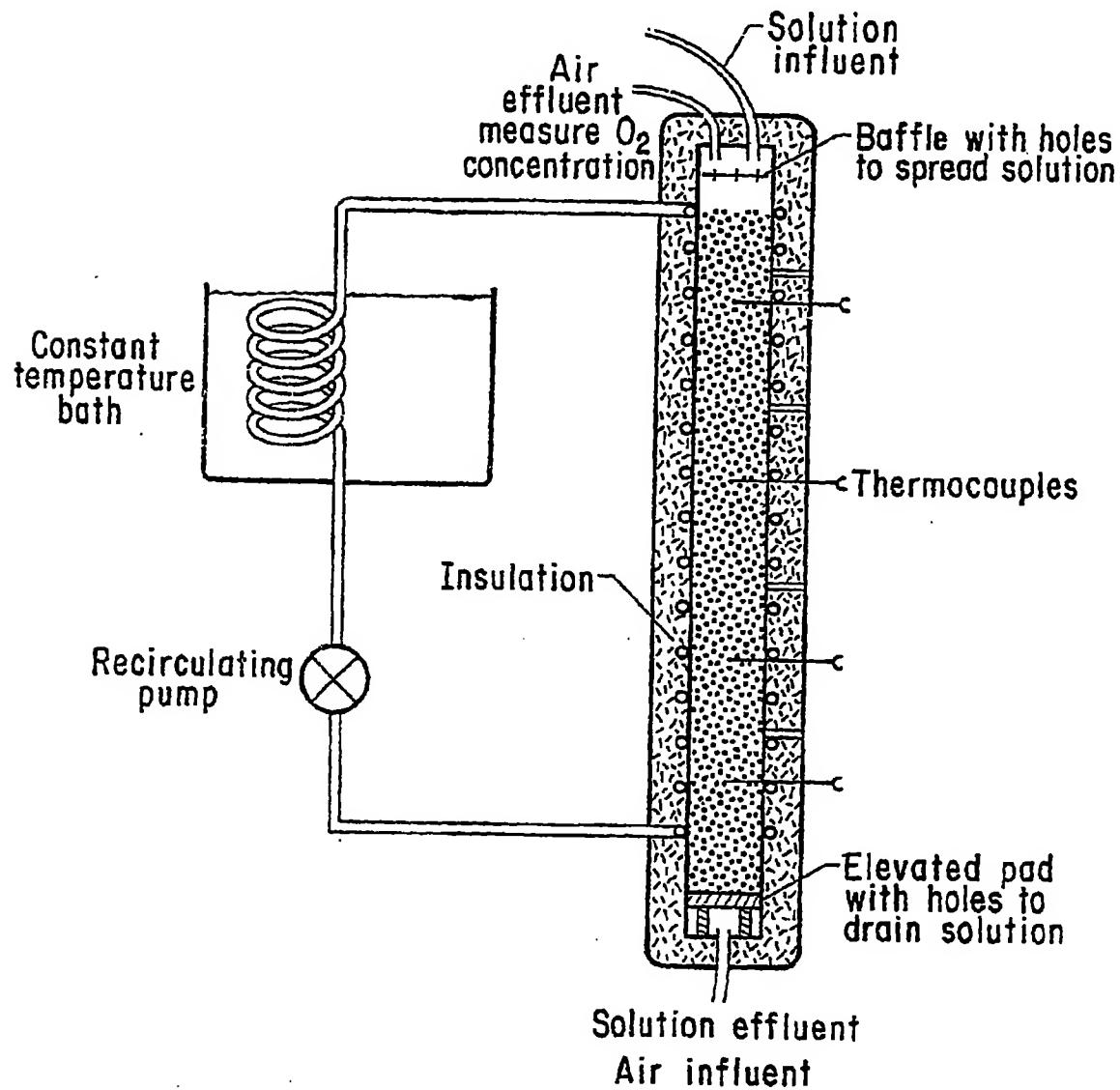


Figure 10 Schematic drawing of a constant temperature leach column. Flush solutions are applied to the top of the column, air is input at the base. Constant temperature is maintained by a constant temperature bath and tubing wrapped around the insulated column. Temperature is measured along the column. Oxygen concentration is measured in the air effluent from the top of the column.

Data on the columns and on the results of leaching are summarized in Tables 11-14. Plots of the fraction of total iron removed as a function of time for the four columns is given in Figure 11. Figure 11 shows that, as expected, the leaching is faster for smaller coal fragments and higher leaching temperature. The Wyoming coal in Column 1 leaches rapidly, as might be expected from its very low pyrite content (see Table 11, and note in equations (3) and (4) that τ_C and τ_D contain the variable K which increases linearly with pyrite content as shown in Table 6). The slow startup time of Column 1 may be related to retention of iron in the organic structure of the Wyoming coal.

It can be seen from Table 11 that a rather large discrepancy exists between the pyrite content estimated from total iron in the HTA and the pyrite content determined from a forms-of-sulfur analysis for pyritic sulfur. The reason for this discrepancy is not clear, since mineralogic analyses of the low-temperature ash consistently only detected pyrite, quartz and calcite, and showed no evidence for the presence of iron-containing mineral phases other than pyrite (FeS_2). A possible explanation is that the coal contains a considerable amount of organically-bound iron.

The post-mortem analyses reported in Table 13 were obtained in the following fashion: Following the completion of a column experiment, the apparatus was dismantled, and the packed bed of coal was removed from the Plexiglass column in an aluminum coring tube so as to preserve the spatial distribution, both lateral and vertical, of the coal particles within the leach column. The core tube was sealed air-tight, and inlet/outlet tubing was attached so that an inert atmosphere of nitrogen gas could be passed through the coal within the core tube. The nitrogen served to prevent coal oxidation and also to enhance moisture removal. The entire core assembly was placed in a large oven and dried for approximately 40 hours at a temperature of 60°C.

After drying, the core tube was divided into five vertical sections, each approximately 6-8 inches in length. The coal contained in each section was sampled for chemical analysis by a micro-channel sampling technique that yielded approximately 50 grams of coal from each section. The coal remaining in the core tube was prepared for microscopic analysis. Each

Table 11. Selected Chemical and Physical Characteristics of Coal Used in Column Leach Studies
(Before Leaching)

Experiment No.	Coal I.D. and (size fraction)	% Moisture	% Ash (lithia)	Forms of Sulfur Analysis (%)			Percent Iron in Coal Calc. from $\times \text{Fe}_2\text{O}_3$	Percent Pyrite from $\times \text{Fe}_2\text{O}_3$	Percent Pyrite Calc. from $\frac{\% \text{Iron}}{\% \text{Pyritic S}}$	Calorific Value				
				In lithia	Pyritic S	Sulfate S				Btu/lb Dry Basis	Btu/lb Dust Basis	Btu/lb		
1	Wyoming Subbit. (+10 mesh - 3/4 in.)	21.80	5.48	0.13	0.02	0.48	0.63	0.3	0.7	0.24	11955	5805		
2	Illinois #6 (+20 mesh - 3/4 in.)	2.93	13.85	0.85	0.40	2.42	3.67	1.7	3.6	1.6	12086	13213		
3	Illinois #6 (+10 mesh - 3/4 in.)	2.93	13.85	0.85	0.40	2.42	3.67	1.7	3.6	1.6	12086	13213		
4	Illinois #6 (+20 mesh - 1/4 in.)	3.74	11.53	0.79	0.37	2.43	3.59	1.4	3.0	1.5	12190	12830		
ASH ANALYSIS														
				SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	MnO	Na ₂ O	P ₂ O ₅	SO ₃	Totals
Illinois #6	52.8	21.1	0.93	17.3							0.25	0.81	2.15	96.25
Wyoming	26.6	14.3	1.20	8.05	4.49	25.1	0.029	0.42	0.30	0.50	19.5	100.49		
PPM in Ash														
Illinois #6	410	Be	Cr	Cu	Ni	Rb	Sr	V	Zn	Zr				
Wyoming	3130	7.	5	160	90	10	2050	210	570	220				

^aAll percents by weight on a dry basis (except moisture).

^a_a $H_{mef} = [Btu/lb moist coal - 50 (\% total S/100 g moist coal)] + 1100 - [1.08 (\% ash/100 g moist coal) + 0.55 (\% total S/100 g moist coal)] \times 100$

^a_a $q_{mef} = [Btu/lb dry coal - 50 (\% total S/100 g dry coal)] + 1100 - [1.08 (\% ash/100 g dry coal) + 0.55 (\% total S/100 g dry coal)] \times 100$

Table 12

OPERATIONAL PARAMETERS FOR COLUMN LEACHING EXPERIMENTS

<u>Column Experiment #</u>	<u>0 C Temperature</u>	<u>Total Leach Time (days)</u>	<u>Leachate Composition/pH</u>	<u>Coal Mass (Kg)</u>	<u>Solution Flush Rate ml/day</u>	<u>Darcy Air Flow Rate (cm/s)</u>	<u>Interblock Porosity**</u>
1	35	365	HCl/1.5	2.18	500	0.0011-0.0015	—
2	35	422	HCl/1.5	2.46	500	0.0011-0.0015	57%
3	50	376	*H ₂ SO ₄ /1.5	2.66	1000	0.0011-0.0015	56%
4	50	379	*H ₂ SO ₄ /1.5	2.61	1000	0.0011-0.0015	56%

*Bacterial inoculation with Thiobacillus ferrooxidans ATCC #13661. (Supplied by Prof. R.W. Stone, Microbiology Dept., Penn State University.)

**Interblock porosity = 1 - $\left(\frac{\text{mass coal}}{\rho \text{ coal}} + \text{column} \right)$; column volume = 3600 cm³

Table 13. Chemical Analyses of Coal Samples After Leaching
in the Column Apparatus

Sample I.D.	Moisture*	Z	% Ash (HTA)	Forms of Sulfur (Z)			Total S	Z Pyrite Calc. from Sulfate S	Calorific Value (BTU/lb)
				Pyritic S	Sulfate S	Organic S			
Column 1									
WY 1-6 (top)	7.03	—	2.32	0.05	0.01	0.42	0.48	0.094	12092
WY 2-6	7.03	—	—	—	—	—	—	12006	11440
WY 3-6	5.41	—	—	—	—	—	—	—	—
WY 4-6	5.29	3.83	0.02	0.00	0.45	0.47	0.038	12047	12324
WY 5-6	6.67	—	—	—	—	—	—	11988	11850
WY 6-6	5.99	2.42	0.03	0.00	0.43	0.46	0.036	12094	12315
WY 7-6 (bot)	5.34	—	—	—	—	—	—	12227	11815
							11934	—	12368
Column 2									
2-1 (top)	2.08	10.5	0.68±0.03	0.06±0.01	2.42	3.16±0.05	1.28	12996	14015
2-2	1.78	8.84	0.65	0.05	2.50	3.20	1.22	12710	13897
2-3	1.99	9.16	0.51	0.05	2.53	3.09	0.96	12650	13854
2-4	1.59	9.70	0.52	0.04	2.51	3.07	0.98	12510	13872
2-5 (bot)	1.89	9.42	0.49	0.05	2.51	3.05	0.92	12592	14096
							14193	—	14466
Column 3									
3-1 (bot)	2.86	7.16	0.45	0.17	2.62	3.24	0.84	12778	13462
3-2	5.24	7.94	0.87	0.19	2.60	3.66	1.63	12518	13074
3-3	5.42	7.75	0.54	0.19	2.60	3.31	1.01	12514	13782
3-4	2.79	7.28	0.38	0.19	2.65	3.22	0.71	12564	13750
3-5 (top)	4.15	7.62	0.37	0.28	2.55	3.20	0.69	12702	13337
							13936	—	13940
Column 4									
4-1 (top)	1.27	10.7	0.20	0.22	2.46	2.88	0.38	12028	13501
4-2	0.89	11.2	0.17	0.22	2.39	2.78	0.32	12774	14694
4-3	1.12	11.0	0.18	0.20	2.38	2.76	0.34	12878	14540
4-4	1.16	9.98	0.15	0.19	2.43	2.77	0.28	12079	13615
4-5 (bot)	0.44	12.5	0.20	0.16	2.45	2.81	0.38	12163	14150

* dried at 60°C under nitrogen for 40^h.

Table 14 Percent Change in Chemical Characteristics
of Coal Leached in the Column Apparatus

Sample <u>I.D.</u>	Ash <u>HTA</u>	Pyrite <u>Content</u>	Organic <u>Sulfur</u>	Total <u>Sulfur</u>	<u>Calorific Value (BTU/lb)</u>		
					<u>dry basis</u>	<u>Mmmf</u>	<u>dmmf</u>
Column 1							
WY 2-6	-57.7	-61.5	-12.5	-24.8	+0.4	+16.7	-2.8
WY 4-6	-30.1	-84.6	- 6.3	-25.4	+0.3	+20.9	-1.3
WY 6-6	-55.8	<u>-76.9</u>	-10.4	-27.0	+2.3	+20.5	-0.8
Column 2							
2-1	-24.2	-20.0	0.0	-13.9	+4.2	+ 6.0	-0.2
2-2	-36.2	-23.5	+ 3.3	-12.8	+5.2	+ 5.2	-1.3
2-3	-33.9	-40.0	+ 4.5	-15.8	+4.7	+ 4.9	-1.4
2-4	-30.0	-38.8	+ 3.7	-16.3	+3.7	+ 5.0	-1.7
2-5	-32.0	<u>-42.4</u>	+ 3.7	-16.9	+4.2	+ 7.4	+0.9
Column 3							
3-1	-48.3	-47.0	+ 8.3	-11.7	+5.7	+ 1.4	-2.8
3-2	-43.4	+ 2.4	+ 7.4	- 0.3	+3.6	- 1.0	-3.9
3-3	-44.0	-35.4	+ 7.4	- 9.3	+3.5	- 1.6	-4.1
3-4	-47.4	-55.3	+ 9.5	-12.3	+4.0	+ 0.9	-4.3
3-5	-45.0	<u>-56.5</u>	+ 5.4	-12.8	+5.1	+ 1.1	-2.8
Column 4							
4-1	- 7.2	-74.7	+ 1.2	-19.8	-1.3	+ 5.2	-2.6
4-2	- 2.9	-78.5	- 1.6	-22.6	+4.8	+13.0	+4.2
4-3	- 4.6	-77.2	- 2.1	-23.1	+5.6	+13.3	+4.8
4-4	-13.4	-81.0	0.0	-22.8	-0.9	+ 4.9	-3.0
4-5	+ 8.4	<u>-74.7</u>	+ 0.1	-21.7	-0.2	+ 9.8	+0.8
-77.2± 2.7							

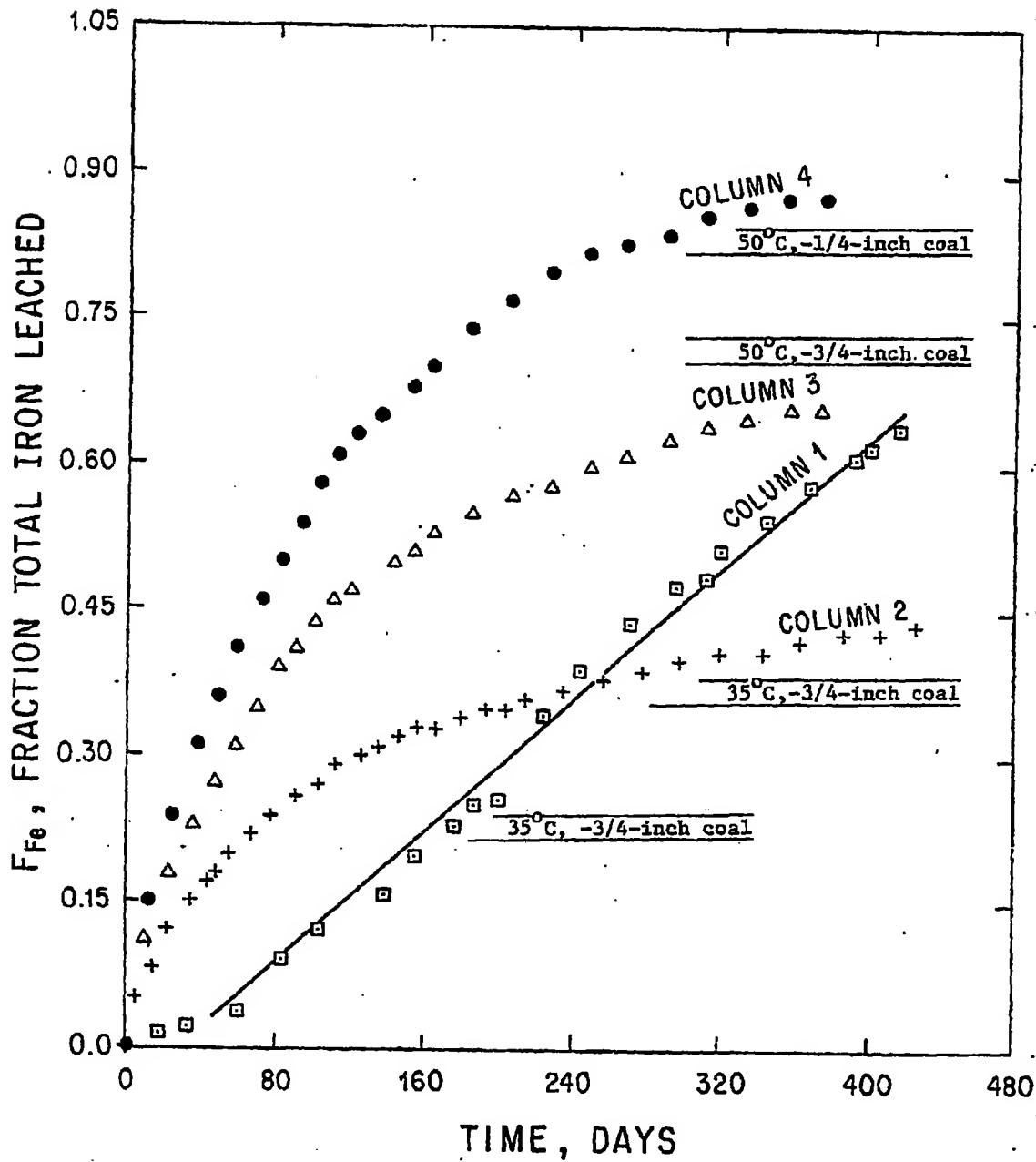


Figure 11 Iron extraction histories for coals leached in extended-duration column experiments. Total iron in solution effluents from the leach columns are ratioed against total iron in the unleached coal (from HTA analysis) to estimate fractional iron removal.

50-gram coal sample was crushed to the appropriate size range for chemical analysis.

Changes in the chemical characteristics of the coal before and after column leaching are most easily interpreted by using Table 14 that reports the effects of leaching on a percent change basis. A minus sign indicates a net decrease and a plus sign a net increase after leaching.

1. The Stoichiometry of Leaching

As in the kettle experiments, the stoichiometry of leaching can be determined from the increase in organic sulfur and the decrease in pyritic sulfur. Note, however that the fate of organic sulfur varies in the four column experiments (Table 14). The Wyoming coal loses organic sulfur, columns 2 and 3 gain organic sulfur, and column 4 shows no change. Table 15 interprets the results for columns 2 to 4. Columns 2 and 3 indicate a stoichiometric X value of 0.6 ± 0.2 .

2. Determination of k_{ox} and D_E

τ_C and τ_D can be determined from the shape of the leach curves if we assume the form of the iron fraction leached vs. time curves (Figure 11) reflect the form of the fraction pyrite leached vs. time curves. It is clear from Table 14 that the fraction iron leached does not accurately reflect the fraction pyrite leached. This is shown also in Figure 12 where pyrite leach curves (heavy dash) have been constructed such that they pass through the total pyrite extracted points and have a similar form to the iron leach curves. The pyrite recovery (dashed curves) lie distinctly below the iron recovery data. The pyrite recovery curves are analyzed in two ways: (1) by the non-linear curve fitting technique used in the kettle experiments, and (2) by simulating the column leach experiments using the finite difference model described and used in the next section.

Shrinking core model curves, fit for two different values of τ_C by a least squares iterative technique to the iron recovery data, are shown in Figure 13. The values of τ_C and τ_D obtained by this fit are corrected for the difference between the iron and pyrite recovery curves by increasing both by the ratio of the total leach time to the leach time at which the

APPENDIX E Experimental Column Leaching of Coal

A. Leach Column Design and Materials

Many variations in column design are reported in the hydrometallurgical literature. In general, the column apparatus is designed to provide as inert a container as possible so that the leaching chemistry of interest may be studied without contamination from the column or accessory hardware. Plastics appear to be best suited for laboratory-scale column leaching applications, both Plexiglass^(R) and PVC^(R) have been used successfully (Brimhall and Wadsworth, 1973; Bruynesteyn and Vizzoly, 1981). Stainless steel columns have been used in one large-scale leaching experiment (Murr, 1980).

Solution flow within the column is a critical operating parameter and to avoid undue wall effects the column diameter (I.D.) should be four times the largest particle diameter in the aggregate of particles being leached (Potter, 1981). Column length is used to size the experiment to handle the desired mass of material. Four leaching columns, identical to the scale drawing in Figure E-1 were constructed using clear acrylic plastic (Plexiglass) tube. The reader is referred to Figure E-1 for dimensions and other details regarding the construction materials. A photograph of the column apparatus and accessory hardware appears in Figure E-2. The clear column allowed visual checks to be made on solution flow, sample compaction, and solution ponding in the bottom of the column. PVC end fittings (pipe clean-outs) were attached (using PVC cement) to the top and bottom of the

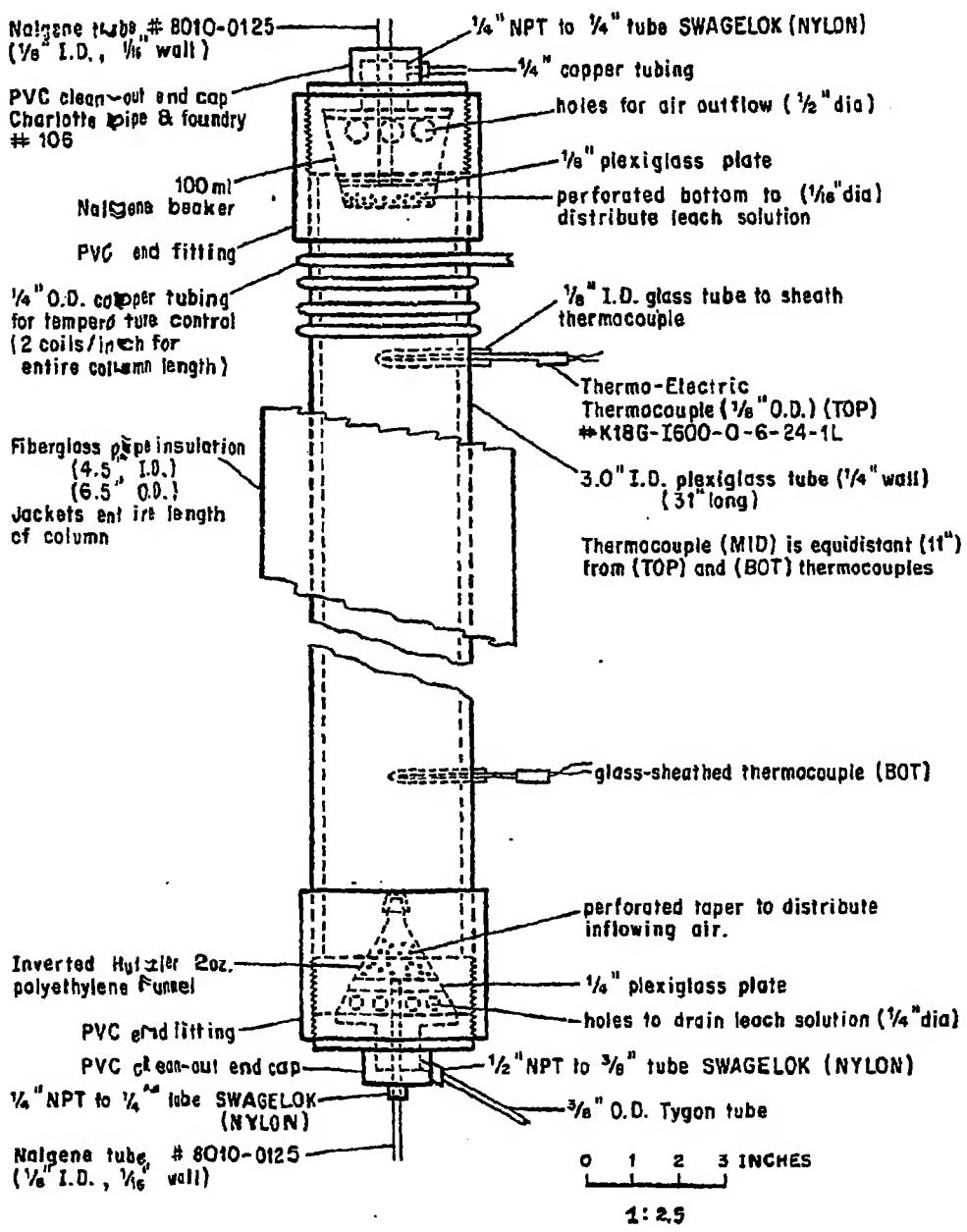
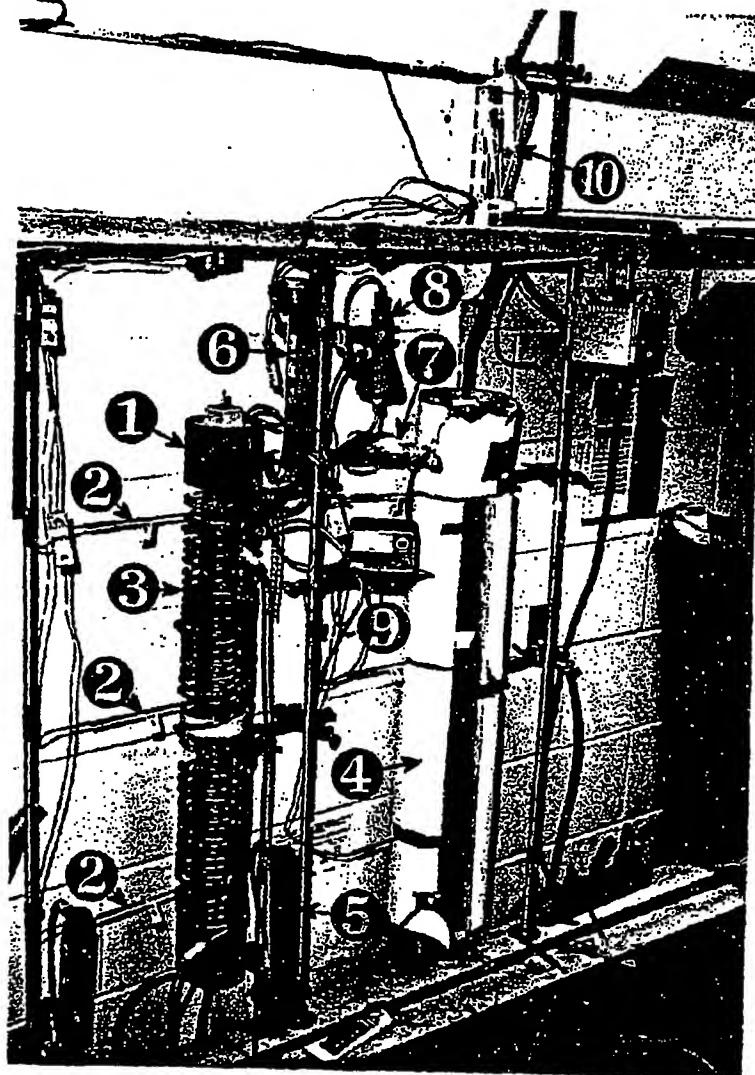


Figure E-1 Design and Construction Materials of the Leaching Column Apparatus (to scale)



Key:

- | | |
|--|--|
| 1. PVC end fittings and caps | 6. Rotameter for outflow air |
| 2. Thermocouples (TOP, MID, BOTTOM) | 7. Drying tube with desiccant |
| 3. Copper tubing for temperature control | 8. O ₂ measurement flask and O ₂ probe |
| 4. Fiberglass insulation jacket | 9. Oxygen meter |
| 5. Rotameter for inflow air | 10. Reservoir for leach solution |

Figure E-2 The Column Leaching Apparatus and Accessory Hardware

Plexiglass tube. The screw-type inserts (PVC end caps) for the end fittings were modified to hold the inlet and outlet tubing and a solution distribution and collection system.

The top-end cap was drilled to accept an inlet tube for leach solution and an outlet tube for effluent air. Nylon Swagelok^(R) compression fittings and Nalgene^(R) tubing were used throughout to maintain an air-tight seal and also prevent corrosion. A 100-ml Nalgene beaker was designed and fit to the top-end cap as a leach solution applicator. Thus, the leach solution was sprinkled evenly at the top of the bed of particles within the column. In a similar fashion, the bottom-end cap was drilled for an inlet air tube and a drainage tube for effluent leachate. An inverted polyethylene funnel was designed and fit to the bottom-end cap. The funnel served to 1) support the sample charge in the column, 2) distribute the air inflow evenly in the column, 3) prevent clogging of the solution outflow with particulates while allowing drainage of effluent solution, and 4) prevent leach solution from collecting in the inflow air line.

The column apparatus was designed so that a constant temperature could be maintained throughout the interior of the column. Copper tube was tightly coiled around the column with a spacing of approximately two coils/inch of column. Distilled deionized water could then be circulated from a constant temperature bath.¹ The temperature of the bath was held constant to a tolerance of $\pm 0.2^{\circ}\text{C}$. Temperatures up to 65°C were envisioned for column experimentation and this necessitated using a submersible pump

¹Tecam model TE-7

unit² for water circulation that was thermally insulated and constructed of a plastic material to prevent corrosion at the high operating temperatures. Fiberglass pipe insulation was used to jacket the column and prevent heat loss.

Temperature in the column was monitored with three glass-sheathed type-K thermocouples. Three holes were drilled in the column and the thermocouples were sealed in place with epoxy cement so that the end of the probe rested in the center of the column. Temperatures at the three thermocouple ports were monitored continuously by incorporating a multi-channel data logger.³ Twelve data channels (3 for each column) were thus dedicated to monitor temperature. Compressed air from a standard laboratory bench outlet was used as a source of air for the column experiments. The bench outlet was modified to accept a compressed air filter⁴ and an air line regulator/pressure gage⁵. The compressed air was metered to a pre-determined flow rate of 0.003-0.004 std. liters/min. (or a Darcy air flow rate of 0.0011-0.0015 cm/s) with a rotameter⁶. Prior to introducing the air in the column it passed into a bubbling tube containing distilled water. This tube was maintained at the experimental temperature to equilibrate the temperature of the gas and to saturate it with water.

²Little Giant Pump Co. model NK-1 #526003

³Monitor Labs model 9300

⁴Model M-20, Motor Guard Corp., Box 1834, San Leandro, CA 94577

⁵Model 282.16036, Sears Roebuck and Co.

⁶Model #1355CC1B1BAA with a R-2-15-AAA tube, Brooks Instrument Div., Emerson Electric Co., Hatfield, PA 19440

Outflowing air first passed through a drying bottle that contained a desiccant⁷ and then into a flask (250 ml Nalgene erlenmeyer) which housed a polarographic probe⁸. The effluent air then passed through a rotameter similar to the one used to meter air inflow. The second (or outflow) rotameter reading could be compared to the inflow rotameter reading to check for air leaks in the column apparatus. Finally, the effluent air passed through a trap containing mineral oil to monitor air outflow qualitatively and prevent back diffusion of air into the O₂ measurement flask or the leaching column.

Measuring the O₂ concentration in the effluent gas stream provided a means of tracking the oxidation reactions taking place between the oxygen in air and the water-saturated coal and pyrite within the column. The polarographic probe responds electrochemically to the oxygen content in the air sample. The current produced by reduction of oxygen at the cathode was input to an oxygen meter⁸ which, in turn, produced a voltage proportional to the oxygen concentration in the effluent gas stream. The oxygen analyzer system had to be calibrated and this involved removing the probe from the measurement flask, allowing it to equilibrate with air in the laboratory, and then the meter was adjusted to read 21% O₂. Meter calibration was checked twice each day and adjusted if necessary. Meter fluctuation due to battery discharge was eliminated by incorporating two 120V AC to 9V DC converters. Thus, the meter could be operated on a continuous basis. The voltage

⁷Drierite (Anhydrous CaSO₄)

⁸Edmont Oxygen Analyzer System, model 60-620, Energetics Science Div. of Becton Dickinson and Co., Elmsford, NY 10523

output from the oxygen meter entered a multi-channel data logger programmed with a pre-calibrated linear conversion from voltage input to percent oxygen.

The data logger produced a record on paper tape at programmed sampling intervals (typically six hours) of the percent oxygen in the air leaving the column. The oxygen probe was rotated between each of the four leach columns every several days.

Leach solution entered the leaching column by gravity flow from a storage reservoir. The solution was applied at predetermined intervals by simply flushing the solution in the reservoir through the packed bed of coal and then collecting the effluent as it drained from the base of the column. Leach solution composition and application rate will be discussed in the section on experimental conditions.

B. Sample Preparation and Analysis

Four column experiments were planned in this study and the coal samples were prepared to provide information on the leaching of pyrite finely disseminated in a coal matrix. Three of the four column experiments were conducted using the Illinois #6 bituminous coal described in Appendix-B. A fourth column experiment was conducted with a Wyoming subbituminous coal. In addition to distinct physical property differences, the greater tendency for subbituminous coal to self-heat and oxidize provided an excellent comparison in leach behavior to the Hi-vol bituminous coal from Illinois.

The leach columns were designed to hold approximately 2.5 kilograms of coal and sample preparation was accordingly less detailed than the procedure for 10-gram samples that appears in Figure 4 of the text. The Wyoming coal did not contain extraneous rock material and therefore was prepared without special hand-picking or float-sink separations. The as-received coal was

crushed to 3/4 inch top size in a chipmunk jaw crusher and the -20 mesh fines removed by sieving. The +20 mesh -3/4 inch size fraction was used for experimentation.

Two 10 kg splits of Illinois coal were taken from the as-received coal. This material contained fragments of clay, shale, and massive pyrite. The macroscopic fragments were removed by hand and the coal was crushed to 3/4 inch top size in a chipmunk jaw crusher. The crushing procedure liberated more massive pyrite from the coal matrix which was again removed by hand. Effort was also placed upon removing the pyrite-enriched fusinite macerals that were characterized by a distinctive bronze coloration and charcoal-like texture. The -20 mesh fines were then removed by sieving. One of the 10 kg splits was used for experimentation at the +20 mesh -3/4 inch size and the other was crushed to 1/4 inch top size. Crushing to 1/4 inch top size again liberated massive pyritic material that was removed by hand. The -20 mesh fines that resulted from the 1/4 inch top size crushing step were removed by sieving, yielding a +20 mesh -1/4 inch coal sample. Sample preparation for analysis is identical to the analytical flowchart that appears in Figure 4 of the text. Selected chemical and physical properties of the coal samples used for the column leaching experiments appear in Table E-1.

Table 5-L Selected Chemical and Physical Characteristics of Coal Used in Column Leach Studies
(Before Leaching)

Column Experiment No.	Coal I.D. and size fraction	Z* Volatue	% Ash (ITA)	Forms of Sulfur Analysis (%)			Percent Iron in Coal Calc. from Calc. from Pyrite	Percent Pyrite	Percent Pyrite	Calorific Value
				Pyritic S	Sulfate S	Total S				
1	Wyoming Subbit. (+20 mesh - 3/4 in.)	21.80	5.48	0.13	0.02	0.48	0.63	0.3	0.7	0.24
2	Illinois #6 (+20 mesh - 3/4 in.)	2.93	13.85	0.85	0.40	2.42	3.67	1.7	1.6	1.6
3	Illinois #6 (+20 mesh - 3/4 in.)	2.93	13.85	0.85	0.40	2.42	3.67	1.7	3.6	1.6
4	Illinois #6 (+20 mesh - 1/4 in.)	3.74	11.53	0.79	0.37	2.43	3.59	1.4	3.0	1.5
ASH ANALYSIS										
				SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O
										K ₂ O
Illinois #6		52.8	21.1	0.93	17.3	1.16	1.97	0.025	0.81	2.15
Wyoming		26.6	14.3	1.20	8.05	4.49	25.1	0.029	0.42	0.30
				Ba	Be	Cr	Cu	Hg	P ₂ O ₅	SO ₃
										Totals
Illinois #6		410	170	70	95	—	—	—	—	98.25
Wyoming		1150	7	5	160	90	10	2050	210	160
									Zn	P ₂ O ₅

* All percents by weight on a dry basis (except moisture)

$$\text{** Btu/lb moist coal} = 50 \left(\frac{\text{Btu/lb dry coal}}{\text{Btu/lb dry coal}} \right) + [100 - (1.08 \times \text{ash}/100 \text{ g moist coal})] \times 100$$

$$\text{*** dmuf} = [\text{Btu/lb moist coal} - 50 \left(\frac{\text{Btu/lb dry coal}}{\text{Btu/lb dry coal}} \right)] + [100 - (1.08 \times \text{ash}/100 \text{ g dry coal})] + 0.55 \left(\frac{\text{total S}/100 \text{ g moist coal}}{\text{total S}/100 \text{ g dry coal}} \right)] \times 100$$

Leaching Conditions:

1. Initial Composition of the Leach Solution and Effluent Solution Analysis

The composition of the leach solution was kept simple and free of iron initially so that effluent iron concentration could be used as a measure of the amount of pyrite solubilized. Distilled water was acidified to a pH of 1.5 with concentrated HCl or H₂SO₄. The acid pH was needed to prevent the hydrolysis of ferric ion and the subsequent precipitation of ferri-hydrite (Fe(III)-hydroxide) inside the column apparatus. The leach solutions were stored at room temperature and were added to reservoirs mounted above the column. In this manner, a known volume of leach solution could flow (gravity-flow) into the leach column at pre-determined flushing intervals.

The chemical composition of the effluent leachate was monitored for total iron by atomic absorption spectrometry. The pH of the effluent solutions was also monitored periodically. The results of the total iron analyses are tabulated at the end of this appendix.

2. Bacterial Innoculation

Iron-oxidizing bacteria are known to catalyze the oxidation of pyrite in aqueous media (Lacey and Lawson, 1970). It is therefore desirable to have iron-oxidizing bacteria present and viable in the column experiments. No effort was made to sterilize or treat the coal samples to kill the naturally occurring bacteria associated with coal and coal pyrite. The two column experiments with sulfuric acid lixiviant were innoculated with an active culture of Thiobacillus ferrooxidans. This was accomplished by adding 10 ml of an aqueous growth media containing the bacteria to the column before

starting the regular percolation leaching. No tests were performed to ascertain whether bacterial cells were present in the effluent leachate. Therefore it is not known whether iron-oxidizing bacteria were active during the column experiments. The columns incorporating the HCl lixiviant were not innoculated with the iron-oxidizing bacteria.

3. Column Operating Parameters

The temperature, the solution flush rate, and air inflow rate were the three experimental parameters subject to adjustment during column leaching. Temperatures of 35 and 50°C were chosen for experimentation because:

- (1) The activity of non-thermophilic iron-oxidizing bacteria is known to be reduced at temperatures above 50°C (Murr, 1980).
- (2) The reaction rate of pyrite and the coal matrix would be at a maximum in this temperature range (relative to temperatures below 35°C). As a result, experiment duration could be lessened and changes to the effluent solution and air chemistry (reflecting the relatively rapid reaction rate) would be more pronounced and easier to measure analytically.

The amount of leach solution used to flush the columns was determined by the practical problems encountered in the manual flush procedure. Leach solutions were applied twice each day and solution volume was determined by the chemical composition of the effluent leachate (i.e., leach rate of the pyrite in the column). The lower temperature column experiments showed low levels of iron in the effluent and a 500 ml/day solution volume was used to flush out the dissolved pyritic iron. Conversely, the effluent solutions from the 50°C column experiments were more concentrated in iron and therefore were flushed with a greater volume of solution each day (1000 ml/day).

To ensure the complete saturation of the coal particles, the column apparatus was flooded with leachate initially. The volume of solution required to fill the column was used to estimate the interblock porosity within the column. The interblock porosity was also computed using coal density. The values agree well and appear in Table E-2. The columns were filled with leachate periodically during the course of the leach experiment to maintain the saturated conditions.

An inflow rate of 0.003 - 0.004 std. liters/min. was selected for metering air into the base of the leaching columns. This flow rate could be measured easily and was slow enough to allow the oxygen concentration in the gas phase to be reduced a measurable amount as it passed through the packed coal bed.

The four column experiments were operated under the conditions that appear in Table E-2.

Table E-2
OPERATIONAL PARAMETERS FOR COLUMN LEACHING EXPERIMENTS

<u>Column Experiment #</u>	<u>0_C Temperature</u>	<u>Total Leach Time (days)</u>	<u>Leachate Composition/pH</u>	<u>Coal Mass (Kg)</u>	<u>Solution Flush Rate ml/day</u>	<u>Darcy Air Flow Rate (cm/s)</u>	<u>Interblock Porosity**</u>
1	35	365	HCl/1.5	2.18	500	0.0011-0.0015	—
2	35	422	HCl/1.5	2.46	500	0.0011-0.0015	57%
E-13	50	376	*H ₂ SO ₄ /1.5	2.66	1000	0.0011-0.0015	56%
4	50	379	*H ₂ SO ₄ /1.5	2.61	1000	0.0011-0.0015	56%

*Bacterial inoculation with Thiobacillus ferrooxidans ATCC #13661. (Supplied by Prof. R.W. Stone, Microbiology Dept., Penn State University.)

** Interblock porosity = 1 - $\left(\frac{\text{mass coal}}{\rho \text{ coal}} \right) \div \frac{\text{column}}{\text{volume}}$; column volume = 3600 cm³

D. Experimental Results

Four extended-duration column leaching experiments were conducted in this study. Column 1 and column 2 were leached for 419 days and 427 days, respectively. Column 3 and column 4 were both operated for 374 days. The results of the analyses for total iron in the effluent leachate along with the percent O₂ in the effluent air stream and temperatures measured at the three temperature ports along each column appear in Table E-3. The total iron in the effluent leachate and the fractional O₂ depletion in the effluent air, relative to the influent air, are summarized graphically for the columns that contained Illinois bituminous coal in Figure E-3.